Rhodium-Catalyzed Carbonylation of 2-Alkynylbenzaldehyde under Water-Gas Shift Reaction Conditions: Formation of Novel Tricyclic Lactones

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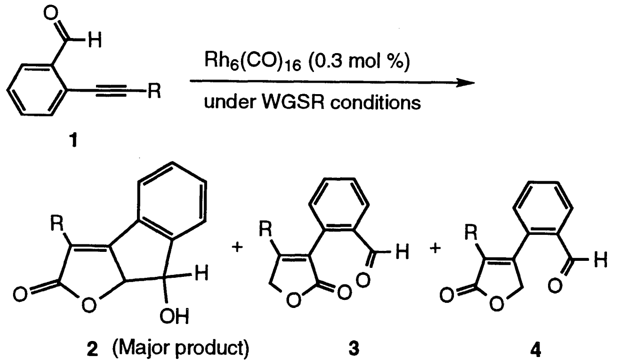
Rhodium complexes catalyze carbonylation of 2-alkynylbenzaldehyde **1** under water-gas shift reaction conditions to give novel lactone **2** as a major product (up to 59% yield), the structure of which is a tricyclic ring system.

Organometallic complex-catalyzed carbonylation under water-gas shift reaction (WGSR) conditions has received much attention.[1] Besides $Fe(CO)_5$[2] and $Ru_3(CO)_{12}$,[3] a rhodium catalyst system[4] has been developed continuously and applied to organic syntheses widely.[5] Recently, we have reported the preparation of 2(5H)-furanones by rhodium-catalyzed reductive carbonylation of alkynes under water-gas shift reaction conditions.[6] We now report that novel tricyclic lactone **2** can be prepared by $Rh_6(CO)_{16}$-catalyzed carbonylation of alkynes having a formyl group adjacent to the carbon-carbon triple bond, such as 2-phenylethynylbenzaldehyde (Scheme 1).

Scheme 1.



(R = Ph, Me, n-Bu, C_6H_4OMe-4, and $C_6H_4CO_2Et$-4)

A mixture of 2-phenylethynylbenzaldehyde **1** (3 mmol), $Rh_6(CO)_{16}$ (0.009 mmol), Et_3N (3 mmol, 0.4 ml) and H_2O (4 mmol, 0.2 ml) in chloroform (45 ml) was placed in a 100 ml stainless steel autoclave under 100 atm of initial carbon monoxide and stirred at 80 °C for 5 h. After removal of the solvent under reduced pressure, the residue was dissolved in ethyl acetate and passed through a column chromatography of silica gel using an eluent of $CH_2Cl_2 : Et_2O = 20 : 1$ to separate the products. The major one among the three kinds of products obtained was recrystallized from ethanol to give 2-oxo-3-phenyl-8-hydroxy-8,8a-dihydro-2H-indeno[2,1-b]furan **2** as colorless crystals (vide infra).

Representative results are summarized in Table 1. The carbonylation of 2-phenylethynylbenzaldehyde (run 1) gave product **2** in 59% yield along with two furanones of by-products **3** (29% yield) and **4** (trace). In this reaction, $[Rh(CO)_2Cl]_2$, $RhCl_3 \cdot xH_2O$ and $RhH(CO)(PPh_3)_3$ showed a definite catalytic activity but a lower selectivity for tricyclic lactone **2**. The best yield was obtained by use of $Rh_6(CO)_{16}$ catalyst in a chloroform solvent.

Table 1. Rhodium-catalyzed carbonylation of 2-alkynylbenzaldehyde under WGSR conditions[a]

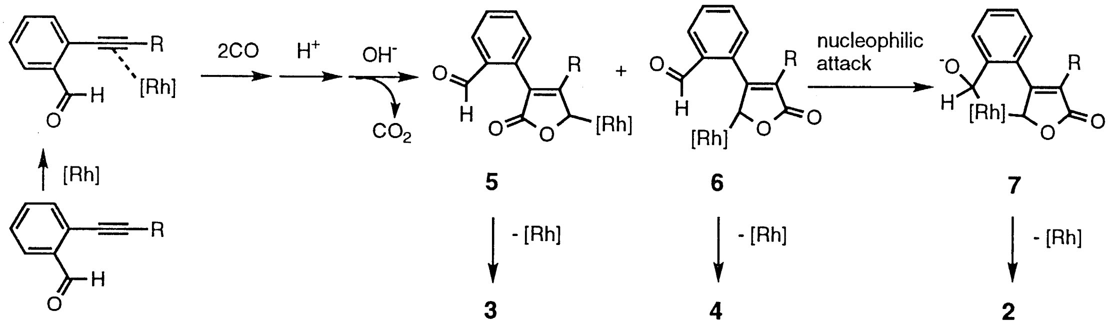
Run	Substrate 1 R	Reaction Time (h)	Yield (%) of Products[b]		
			2	3	4
1	Ph	5	59	29	Trace
2	Me	30	50	34	11
3	n-Bu	40	37	52	5[c]
4	$C_6H_4CO_2Et$-4	8	54	32	Trace
5	C_6H_4OMe-4	10	44	45	7[c]
6[d]	H	10	0	0	0

[a] Reaction conditions: 2-alkynylbenzaldehyde, 3 mmol; $Rh_6(CO)_{16}$, 0.009 mmol; Et_3N, 0.4 ml; H_2O, 0.2 ml; $CHCl_3$, 45 ml; CO, 100 atm; at 80 °C. [b] Determined by HPLC. [c] Isolated yield. [d] Some oligomeric products were detected by GPC.

The carbonylation of 2-methylethynylbenzaldehyde and 2-butylethynylbenzaldehyde under the same reaction conditions, however, proceeded very slowly (runs 2 and 3). The latter gave a lower selectivity for tricyclic lactone (37% yield). Formation of tricyclic lactone was not detected when a terminal acetylene, 2-ethynylbenzaldehyde, was applied. The reactions of 2-phenylethynylbenzaldehyde derivatives having a substituent at the 4-position of the phenyl group gave the corresponding tricyclic products in 54% and 44% yields (runs 4 and 5).

The structures of by-products **3** and **4** were confirmed by the IR, mass, ^1H (270 MHz) and ^{13}C NMR, and NOE spectral analyses as well as by the comparison with the spectral data of furanones.[7] The structure of **2** having the same mass number as **3** and **4** was inferred from the analytical and spectral data.[8] Different from products **3** and **4**, an absorption due to ν (OH) was found around 3540 cm^{-1} in the IR spectrum of **2**. In addition, a doublet peak assignable to be a hydroxyl proton at 3.08 ppm disappeared when a drop of D_2O was added to an NMR sample. Finally, the structure of **2** was determined by an X-ray crystallographic analysis to be a tricyclic skeleton, 2-oxo-3-phenyl-8-hydroxy-8,8a-dihydro-2H-indeno[2,1-b]furan.[9] The ORTEP drawing is illustrated in Figure 1, showing the novel skeleton consisting of one six-membered ring and two five-membered rings definitely in a plane. It is noteworthy that such a tricyclic ring system could be constructed by a one-step reaction of acetylenic substrates which can be prepared easily by a palladium-catalyzed cross-coupling of aryl halides with terminal acetylenes.[10]

Scheme 2.



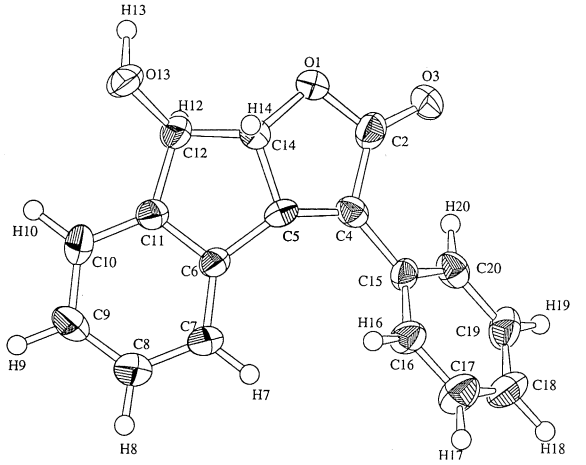


Figure 1. ORTEP drawing of the molecule structure of 2-oxo-3-phenyl-8-hydroxy-8,8a-dihydro-2H-indeno[2,1-b]furan. Important interatomic distances (Å) and angles (°): O(1)-C(2) 1.373(9), C(2)-O(3) 1.215(8), C(1)-C(4) 1.48(1), C(4)-C(5) 1.346(9), C(5)-C(6) 1.463(10), C(6)-C(11) 1.403(9), C(11)-C(12) 1.522(10), C(11)-H(12) 1.00, C(12)-O(13) 1.420(8), O(13)-H(13) 1.04; C(2)-O(1)-C(14) 107.6(6), O(3)-C(2)-O(1) 119.8, O(1)-C(14)-C(15) 105.3(6), C(5)-O(14)-C(12) 104.1(6), O(13)-C(12)-C(14) 114.6(7), C(12)-O(13)-H(13) 106.8.

Although it is not clear at the present time, the mechanism of the formation of **2** should be of particular interest because this is the first example that a formyl group was participated in the carbonylation reaction of acetylenes. When D_2O was used instead of H_2O, dueterated **2**, 2-oxo-3-phenyl-8-hydroxy-8-hydro-8a-dueterio-2H-indeno[2,1-b]furan, was obtained. Taking account of this fact and basing on the previously proposed mechanism for the formation of 2(5H)-furanones from alkynes,[7] we propose a tentative reaction route shown in Scheme 2. A monomeric anionic rhodium complex formed by the coordination of alkyne undergoes insertion of two CO, followed by the attack of H^+ and OH^- to give two precursors, **5** and **6**. Accompanied with elimination of [Rh] from precursors **5** and **6**, furanones **3** and **4** may be formed generally (see ref. 7). Because the rhodium is situated at the place near to the carbonyl group in **6**, however, a nucleophilic attack of the rhodium to the carbonyl group of the formyl substituent will result in the formation of intermediate **7** leading to novel tricyclic lactone **2**. In our previous work[6,7] of furanone synthesis from alkynes, furanones like **3** and **4** as resultant products were obtained in the ratio of about 50:50. The fact that the present reaction yielded a trace of product **4** (see Table 1) supports the proposed reaction route, in which **6** may be a precursor of both **2** and **4**. Further studies are in progress in order to establish the mechanism and extend the scope of this interesting reaction.

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References and Notes

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8 Data for 2-oxo-3-phenyl-8-hydroxy-8,8a-dihydro-2H-indeno[2,1-b]furan: IR(KBr): 3535 cm^{-1} (ν_{OH}), 1756 cm^{-1} (ν_{CO}); ^{1}H-NMR (270 MHz, CD_2Cl_2) δ 7.85-7.26 (m, 9H), 5.40 (d, 1H, J = 5.3 Hz), 5.10 (dd, 1H, J = 5.0 and 5.3 Hz), 3.15 (d, 1H, J = 4.9 Hz); MS: m/z 264 (M^+); Anal. Found: C 77.41; H 4.42%. Calcd. for $C_{17}H_{12}O_3$: C 77.26; H 4.58%.

9 Crystal data for 2-oxo-3-phenyl-8-hydroxy-8,8a-dihydro-2H-indeno[2,1-b]furan: $C_{34}H_{24}O_6$, M=528.56, crystal dimensions 0.7 × 0.15 × 0.25 mm, monoclinic, space group $P2_1/a$(#14), a=10.411(2), b=31.907(7), c=7.632(2)Å, β=93.84(2)°, V=2529.6(9)$Å^3$, Z=4, D_C=1.388 g/cm^3, graphite monochromated MoKα radiation with λ=0.7107 Å, μ(MoKα)= 0.9 cm^{-1}. 6543 reflections were collected at 20 °C on a Rigaku AFC-5FOS four circle diffractometer in the ω-2θ scan mode to $2\theta_{max}$= 55.0 °. The structure was solved by direct methods and expanded using Fourier techniques, and refined to give R= 0.040, R_w= 0.082 for 2138 observed reflections ($F>3\sigma F$).

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